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David C. Look

Wright State University - Main Campus, david.look@wright.edu

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The electrical characterization of semi-insulating GaAs: A correlation with mass-spectrographic analysis^{a)}

D. C. Look

Physics Department, University of Dayton, Dayton, Ohio 45469
(Received 23 May 1977; accepted for publication 4 August 1977)

The room-temperature electrical properties of 28 semi-insulating GaAs crystals have been determined by using a mixed-conductivity analysis. It is shown that for most of these samples, such an analysis gives good accuracy for the electron mobility μ_n and electron concentration n , but poorer accuracy for the hole mobility μ_p , hole concentration p , and intrinsic concentration n_i . The intrinsic concentration is determined at 296°K to be $n_i \approx (1.7 \pm 0.4) \times 10^6 \text{ cm}^{-3}$, which compares favorably with the theoretical value deduced from the band gap and the effective masses. From a Fermi-level analysis, the dominant Cr acceptor is found to lie at $0.69 \pm 0.02 \text{ eV}$ from the valence band. For many of the samples, the ionized-impurity concentrations N_i have been estimated from spark-source mass-spectrographic measurements and are compared with the concentrations predicted from μ_n . In general, the expected inverse relationship between μ_n and N_i is found to hold, but the scatter in the data is quite large, mainly due to the uncertainties in the mass-spectrographic results.

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I. INTRODUCTION

Semi-insulating GaAs, usually produced by doping with Cr and/or O, is of high technological importance because of its usefulness as a substrate material for certain GaAs devices, e.g., FET's. However, in many cases device problems have been shown to be related to the particular substrate used¹; and, furthermore, it appears that some substrates work well under certain fabrication conditions and poorly under others. Thus, it is important to be able to accurately measure parameters which might correlate with substrate performance, e.g., electrical parameters. In this paper we do an extensive analysis of the electrical properties of semi-insulating GaAs, mainly GaAs:Cr. The measurement of these properties is complicated by mixed conduction, i.e., appreciable conduction by both holes and electrons,^{2,3} and we will discuss which electrical parameters can be measured well under these conditions. Finally, we will look at some results of spark-source mass spectroscopy (SSMS) and discuss how well the electron mobility relates to the ionized impurity content deduced by SSMS.

II. EXPERIMENTAL CONSIDERATIONS

The samples used in this study were <100> wafers received from eight different manufacturers (designated A, B, C, etc.).⁴ To the best of our knowledge, the samples designated A, B, and E were grown by the liquid-encapsulated Czochralski (LEC) method, while the rest of the samples were grown basically by the horizontal Bridgman (HB) technique. The crystals were cleaved to typical rectangular dimensions of about $10 \times 4 \times 0.5 \text{ mm}$, and five Ohmic indium contacts were soldered onto one surface in a standard Hall configuration.⁵ (The shorting of the Hall voltage due to the large-area current contacts was accounted for in the calculations.) Prior to being contacted, the samples were etched in 1:1:50 :: H_2SO_4 :30% H_2O_2 : H_2O , and, after contacting, they were degreased in trichlorethy-

lene, acetone, isopropyl alcohol, and deionized water. It is extremely important to ensure clean surfaces because even a small amount of surface conduction can shunt the very high bulk resistance. This was the reason for the "curvature" around room temperature in the n -, p -, and n_i -vs- T^{-1} curves in Ref. 2, and probably those in Ref. 6; we believe the same problem may exist in some of the samples used in this study, although to a much lesser extent.

The electrical-measurement apparatus, which has been described earlier,² was fully guarded and capable of measuring resistances as high as $10^{14} \Omega$, much higher than the maximum sample resistance of about $10^{10} \Omega$. The electrical measurements were carried out in a He exchange-gas Dewar, and the samples were allowed to equilibrate for more than 1 h before any measurements were made. Typical electric fields and current densities were about 1 V/cm and 10^{-8} A/cm^2 , respectively, and the magnetic field was varied between 0 and 18 kG.

III. DATA ANALYSIS

Most GaAs:Cr crystals exhibit mixed conduction which makes it necessary to measure not only the zero-field Hall coefficient R_0 and resistivity ρ_0 , but also their magnetic field B dependences. It was shown in Ref. 2 that the following relationships hold if the magnetic field dependences of R and ρ are due entirely to mixed conduction:

$$\mu_n = \frac{1 + \beta^{-1}}{1 - b^{-1}} (-R_0)\sigma_0, \quad (1)$$

$$\mu_p = \mu_n/b, \quad (2)$$

$$p = \frac{1}{e(-R_0)} \frac{(1 - b^{-1})}{(1 + b^{-1})} \frac{b(1 + \beta b^{-1})}{(1 + \beta)(1 + \beta^{-1})}, \quad (3)$$

$$n = cp = \frac{1}{e(-R_0)} \frac{(1 - b^{-1})}{(1 + b^{-1})} \frac{(\beta + b^{-1})}{(1 + \beta)(1 + \beta^{-1})}, \quad (4)$$

$$n_i = (np)^{1/2}, \quad (5)$$

where

$$b = \frac{1}{2}[A + (A^2 - 4)^{1/2}], \quad (6)$$

^{a)}Work performed at Avionics Laboratory, Wright-Patterson Air Force Base, under contract No. F33615-76-C-1207.

$$c = \frac{1 + b\beta}{b(b + \beta)}, \quad (7)$$

$$A = \frac{2 + T + T/\beta^2}{1 - T/\beta}, \quad T = \frac{(R_0\sigma_0)^2}{S_p}. \quad (8)$$

Here, S_p is the slope of a $(1/B^2)$ -vs- $(\rho_0/\Delta\rho)$ plot, β is the x -axis intercept of an R -vs- $(\Delta\rho/\rho_0)$ plot, and the other symbols have their usual meanings. Unity Hall factors have been assumed, although, if known, they can be entered explicitly, as shown in Ref. 2.

To identify the degree of precision to which each of the quantities in Eqs. (1)–(5) can be calculated, it is necessary to consider their sensitivity to errors in the measured parameters R_0 , σ_0 , S_p , and β . All of the samples examined in this study had negative (n -type) Hall coefficients (i. e., $R_0 < 0$), and all but four had positive β 's. Since $0 < T/\beta < 1$ (for positive β), it can be seen from Eq. (8) that an error in R_0 , σ_0 , S_p , or β will vary the numerator and denominator of A in opposite ways, such as to lead to a larger percentage

error in A , and thus in b , by Eq. (6). (In general, $A \gtrsim 6$, so $b \approx A$.)

Now consider the quantities μ_n , μ_p , n , p , and n_i . From Eq. (1), it is seen that as long as $b \gg 1$, an error in b will not strongly affect μ_n . Furthermore, errors in R_0 , σ_0 , or β will vary both the numerator and denominator of μ_n in the same direction and thus somewhat mitigate the effects of such errors. Similarly, n , given by Eq. (4), is not strongly dependent upon b . The quantities p and μ_p , on the other hand, will vary approximately as the first power of b , and n_i as the square root. Thus, for positive β and $b \gg 1$, it can be concluded that μ_n and n can be calculated to an accuracy as good as (or better than) that of the measured quantities, while μ_p , p , and, to a lesser extent, n_i can have much larger errors, due to their stronger dependences upon b . Specific examples will be given later. However, the problem in calculating μ_p , p , and n_i can be overcome to a certain extent by instead dealing with the product $p\mu_p$,

TABLE I. Calculated electrical parameters for the semi-insulating GaAs samples used in this study.

Sample	ρ_0 ($10^9 \Omega \text{ cm}$)	$-R_0\sigma_0$ ($10^3 \text{ cm}^2/\text{V sec}$)	μ_n ($10^3 \text{ cm}^2/\text{V sec}$)	μ_p ($10^2 \text{ cm}^2/\text{V sec}$)	n (10^6 cm^{-3})	p' (10^6 cm^{-3})	n_i' (10^6 cm^{-3})	$\epsilon_C - \epsilon_F$ (eV)
A ₁	1.63	1.09	3.35	6.60	0.501	5.39	1.64	0.701
A ₂ ^a	1.21	1.86	3.41	8.44	0.963	4.70	2.13	0.684
A ₃	1.04	0.200	2.60	3.31	0.258	13.3	1.86	0.718
A ₄	1.69	0.767	2.82	8.45	0.575	5.17	1.72	0.697
B ₁ ^a	0.335	3.09	5.73	17.2	2.10	16.5	5.89	0.664
B ₂	0.697	2.80	5.85	8.42	0.832	12.5	3.23	0.688
C ₁ ^a	0.930	2.10	3.67	5.51	1.15	6.21	2.67	0.680
C ₂	0.634	0.125	2.82	2.83	0.460	21.4	3.14	0.703
C ₃ ^a	0.733	2.45	2.94	4.90	2.48	3.04	2.74	0.660
C ₄	0.0194	0.019
C ₅	1.20	2.20	4.39	5.40	0.658	5.79	1.68	0.694
C ₆ ^a	1.13	2.71	4.39	9.69	0.868	4.32	1.94	0.687
C ₇ ^a	0.957	2.27	3.10	1.13	1.69	3.21	2.11	0.670
C ₈	1.19	2.25	3.02	8.36	1.39	2.64	1.92	0.675
D ₁	0.0645	5.74	5.74	...	16.9	0.611
E ₁	0.843	0.767	4.73	5.55	0.392	13.9	2.33	0.707
E ₂	1.18	1.84	4.65	7.81	0.549	6.83	1.94	0.699
F ₁	0.927	2.31	4.33	11.1	0.978	6.26	2.47	0.684
F ₂	0.897	2.77	4.43	5.19	1.04	5.84	2.46	0.682
F ₃ ^a	0.0630	2.02	3.72	23.9	19.2	69.3	36.5	0.608
F ₄ ^a	0.355	2.58	3.28	8.07	4.44	7.54	5.79	0.645
F ₅	1.36	1.28	4.32	6.77	0.419	7.00	1.71	0.706
F ₆	1.21	1.49	4.40	4.77	0.332	9.21	1.75	0.711
G ₁ ^a	0.794	2.75	4.82	6.38	1.01	7.45	2.74	0.683
G ₂ ^a	0.522	2.97	4.14	3.44	2.14	7.80	4.08	0.664
H ₁	0.961	1.19	4.40	4.21	0.492	10.8	2.31	0.701
H ₂	0.786	0.385	4.03	4.03	0.350	16.3	2.39	0.710
H ₃	1.21	1.14	4.04	5.89	0.494	7.92	1.98	0.701

^aGreater than 10% uncertainty in the value of β .

TABLE II. Error analysis for three representative samples (all units are %). For part (a), a systematic error $\Delta\rho_0 = +10\%$ is assumed. For part (b), random errors of 5% in ρ_0 , R_0 , β , and S_p are assumed.

Sample	$\Delta\mu_n$	$\Delta\mu_p$	Δp	Δn	Δn_i
(a) H ₂	-6	+22	-27	+7	-12
H ₃	-4	+24	-27	-5	-17
B ₂	-4	+27	-28	-6	-18
(b) H ₂	5	19	22	13	7
H ₃	4	21	27	7	12
B ₂	3	23	27	4	13

$$p\mu_p = \frac{\sigma_0}{e} \frac{(1 + \beta b^{-1})}{(1 + \beta)(1 + b^{-1})}. \quad (9)$$

This quantity does not depend strongly upon b , and, in fact, errors in β or b vary the numerator and denominator in the same direction. It is a useful quantity because the typical impurity concentrations in semi-insulating GaAs crystals should not change μ_p significantly from its lattice-limited mobility.⁷ Thus, in many cases, a more accurate value of p can be determined by using Eq. (9) with the assumption of a constant $\mu_p \approx 400 \text{ cm}^2/\text{V sec}$. Then, since n can be calculated with reasonable accuracy, as shown above, a good value of $n_i = (np)^{1/2}$ may be obtained. The value of n_i should, of course, be a constant at a given temperature and is a good check on the overall accuracy of the calculations for each sample. From the known effective masses ($m_n \approx 0.068m_0$ and $m_p \approx 0.5m_0$) and the room-temperature band gap [$E_g(296^\circ\text{K}) \approx 1.424 \text{ eV}$],⁸ we can calculate⁵ a theoretical value $n_i \approx 1.5 \times 10^6 \text{ cm}^{-3}$. Any experimental value of n_i significantly different from this might indicate one of the following problems: (1) surface conduction, which will raise the measured σ_0 and might also affect R_0 , β , and S_p ; (2) inhomogeneities, which will cause an increase of R with B , and thus increase β , and which again may also affect the other quantities; (3) single-carrier contributions to β and S_p , which should be negligible for most of these samples²; (4) large random errors, which occur primarily if the dependence of either R or $\Delta\rho/\rho_0$ on B is very weak. It should be noted that the temperature dependence of n_i is quite large, greater than $0.2 \times 10^6 \text{ cm}^{-3}/^\circ\text{K}$ in the room-temperature region; therefore, a scatter of about $0.4 \times 10^6 \text{ cm}^{-3}$ in the measured values of n_i is certainly reasonable due to this cause alone. This problem will be addressed in more detail later.

The measured and calculated electrical parameters are presented in Table I. The samples are designated by manufacturer⁴ and number; e.g., A₂ denotes manufacturer A, sample No. 2. The values of μ_n , μ_p , and n were calculated from Eqs. (1)–(5), with no added assumptions, while p' and n_i' were calculated from Eqs. (9) and (5), with the assumption $\mu_p \approx 400 \text{ cm}^2/\text{V sec}$. The room-temperature Fermi level was calculated from⁹

$$\epsilon_C - \epsilon_F \approx 0.0255 \ln[(4.37 \times 10^{17})/n]. \quad (10)$$

Typically, the random errors in ρ_0 , R_0 , S_p , and β were about 5%, although in some samples, designated

in Table I by a superscript a, the values of β were much more uncertain. However, as we will show below, there also appeared to be some systematic errors, especially in ρ_0 . In Table II are presented the results of assuming either a systematic error of 10% in ρ_0 or random errors of 5% in ρ_0 , R_0 , S_p , and β . The samples represented, H₂, H₃, and B₂, cover a wide span of ($R_0\sigma_0$) and β . It is clearly seen that, as argued earlier, the values of μ_n and n are quite precise, while the values of μ_p and p are much more uncertain. Furthermore, it is seen that for a systematic error in ρ_0 , the induced errors in p and μ_p are of opposite sign and nearly equal magnitude, so that the product $p\mu_p$ is much more precise, as expected. Qualitatively, much the same results are realized if a systematic error is assumed in R_0 , S_p , or β . We could also consider various combinations of systematic errors, but this would become quite speculative.

To check these ideas, sample E₂ was measured several times, sometimes after conditions of heating (to 420 °K) and light irradiation, over a period of about six months. The maximum variation of n from its mean was about 7%, μ_n about 2%, p about 53%, μ_p about 33%, and n_i about 33%. The relative magnitudes of the variations are in rough agreement with what might be expected from Table II and confirm the precision of the measured n and μ_n .

The value of n_i (or n_i') should be a constant and should not correlate with any other quantity. However, there is a correlation with ρ_0 , as shown in Fig. 1, and the tail of this curve, at least, cannot be accounted for by variations in room temperature. Again referring to Table II, we can infer that if the apparent ρ_0 is too low, for some reason, then the apparent n_i will be too high, other things being equal. A good candidate for causing this is surface conduction. We have found that etching and degreasing a sample often raises its resistivity significantly. Possibly our cleaning procedure is not adequate to totally eliminate surface conduction in all of the samples. Another possibility is that, at the lower resistivities, mechanisms other than mixed conductivity are contributing to the magnetic field dependence of R and ρ . This is supported by the fact that these dependences are more uncertain for the samples having large apparent n_i 's. A third possible explanation of the problem is the existence of long-lived traps, which keep one or both of the carrier concentrations above their thermal-equilibrium values for long periods of time (several hours). We have seen such an effect after light irradiation, and it occurs predominantly in those samples having apparent values of n_i which are too high.

Whatever the mechanism is, it seems to affect primarily the measured hole concentrations. Thus, as mentioned earlier, in three measurements of sample E₂ over a period of several months, n_i' decreased from 2.77×10^6 to $1.93 \times 10^6 \text{ cm}^{-3}$, mainly due to a large decrease in p , because n and μ_n remained unchanged to within 7 and 2%, respectively.

One way to minimize the aforementioned surface-conduction effects is to go to higher temperatures, since the bulk resistivity decreases very rapidly with

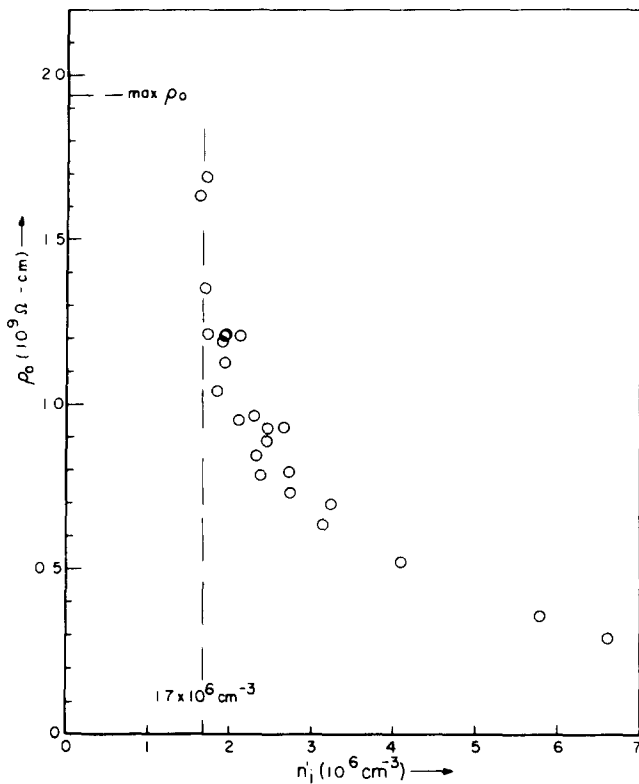


FIG. 1. The measured resistivity ρ_0 versus the calculated intrinsic concentration n_i' . The theoretical maximum ρ_0 is shown under the assumptions $\mu_n \approx 3000$ and $\mu_p \approx 300 \text{ cm}^2/\text{V sec}$.

temperature. This was done in the work described in Ref. 2. However, such a requirement reduces the convenience of these measurements and thus their value as a characterization tool. Furthermore, even at room temperature, as we have shown above, the values of μ_n and n should still be fairly reliable, and these are the important parameters for relating to impurity concentration.

It is seen in Fig. 1 that the values of n_i' at high ρ_0 tend toward an asymptotic value of about $(1.7 \pm 0.4) \times 10^6 \text{ cm}^{-3}$. This value compares very favorably with the theoretical value calculated earlier from the room-temperature (296°K) band gap. It is important to have a good room-temperature value of n_i because of its importance in diffusion studies¹⁰ and certain device calculations,¹¹ among other things. Also shown in Fig. 1 is the theoretical maximum resistivity $\rho_{\max} = [2en_i(\mu_n\mu_p)^{1/2}]^{-1} \approx 1.9 \times 10^9 \text{ } \Omega \text{ cm}$, calculated by using values of $\mu_n \approx 3000$ and $\mu_p \approx 300 \text{ cm}^2/\text{V sec}$. For higher-mobility material, ρ_{\max} would be somewhat lower than this, but it is apparent that much of the commercially available semi-insulating GaAs is within a factor of 2 of its maximum theoretical resistivity.

Several other observations may be made from the data of Table I. For example, the fact that Hall measurements in GaAs:Cr crystals almost always indicate n type, and thermoprobe measurements, p type,¹² is easily explained by the results of this study; i.e., all of the crystals have negative Hall coefficients, but yet all of the Cr-doped crystals also have $p > n$ (sample D₁,

the lone exception, is O doped). The high mobility ratio μ_n/μ_p pulls R_0 to negative values.

Another observation is that the actual electron mobility μ_n is much different, in most cases, than the apparent mobility, $R_0\sigma_0$, as would be deduced from a simple Hall measurement. Thus, the mixed-conductivity analysis is quite necessary here to get reliable values of electron mobility and concentration.

A third observation concerns the measured Fermi levels which appear to be distributed within a rather narrow energy range. From a simple model of this distribution we can determine the room-temperature Cr energy level. The fraction of ionized Cr acceptors (compensation ratio for the acceptors) is given by

$$K = \frac{N_{AA}^-}{N_{AA}} = \left(1 + g_V \exp \frac{(\epsilon_{AA} - \epsilon_F)}{kT}\right)^{-1}, \quad (11)$$

where g_V is the degeneracy factor and ϵ_{AA} and ϵ_F are the Cr (or deep acceptor) level and Fermi level, respectively, measured with respect to the conduction band. Let $\epsilon \equiv \epsilon_F - \epsilon_{AA}$. Then we can define density of state functions $N(\epsilon)$ and $\gamma(K)$ such that $N(\epsilon)d\epsilon = \gamma(K)dK$, where $N(\epsilon)d\epsilon$ is the number of samples having energy between ϵ and $\epsilon + d\epsilon$ and $\gamma(K)dK$ is the number of samples having a compensation ratio between K and $K + dK$. Now, if $K \approx 0$, the sample will be high-conductivity p type, and if $K \approx 1$, n type. Within a given Cr-doped boule there will often be high-conductivity regions, especially at the ends. These parts are discarded, of course, but "good" wafers cut from near the discarded regions may have K 's near 0 or 1.

The point here is that a cross section of commercially obtained semi-insulating GaAs samples may have K values ranging from, say, about 0.1 to 0.9. In the absence of more complete information, we could assume, as a first approximation, a uniform distribution over this range of K . Then $\gamma(K) = N_T(K_u - K_l)^{-1} = 32.5$ in this case, since $N_T = 26$ (total number of Cr-doped samples), and we have assumed $K_u = 0.9$ and $K_l = 0.1$. Finally, we use Eq. (11) to write dK in terms of $d\epsilon$, and get

$$N(\epsilon)d\epsilon = \frac{N_T}{(K_u - K_l)kT} \frac{g_V \exp(-\epsilon/kT)}{[1 + g_V \exp(-\epsilon/kT)]^2} d\epsilon. \quad (12)$$

We first note that $N(\epsilon)$ has a maximum at $\epsilon = \epsilon_F - \epsilon_{AA} = kT \ln(g_V)$. For monovalent acceptors near the valence band, we would have $g_V = 4$, and we will, for the lack of better information, assume that this value obtains even for our deep acceptor. Then, at room temperature, the maximum in $N(\epsilon)$ occurs at $\epsilon_F - \epsilon_{AA} \approx 0.035 \text{ eV}$. To form a reasonable histogram, we let $d\epsilon = 0.02 \text{ eV}$, and find, from Table I, that the maximum number of samples fall in the bar centered at $\epsilon_F = -0.69 \text{ eV}$, giving $\epsilon_{AA} = -0.73 \text{ eV}$. An error of $\pm 0.02 \text{ eV}$ is reasonable here, considering the uncertainty of g_V and the somewhat arbitrary nature of forming the histogram.

The experimental and theoretical histograms are plotted in Fig. 2. From the experimental histogram, it is seen that a better choice of the K range might have been 0.2–0.95, but this does not affect the shape of

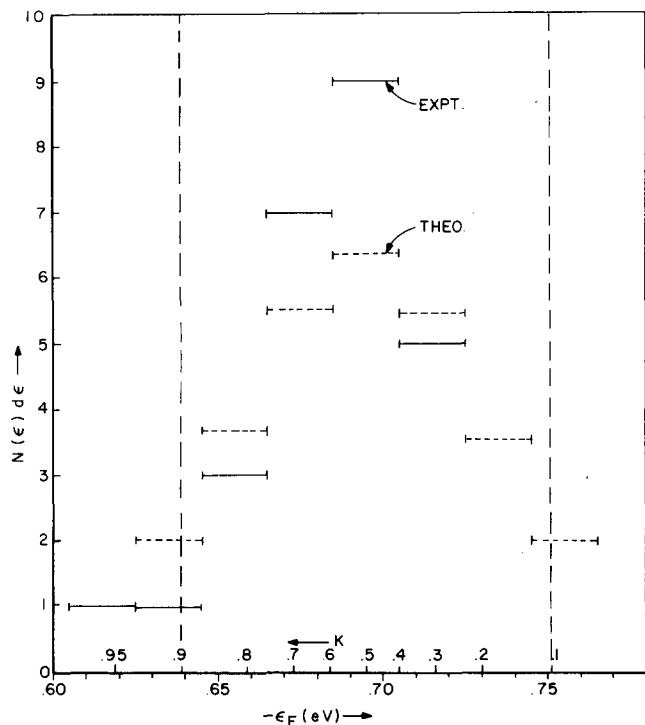


FIG. 2. The experimental (solid line) and theoretical (dotted line) density-of-states histograms in ϵ space for the model described in the text. The distribution in K space is assumed to be uniform between $K=0.1$ and 0.9 . Here $\epsilon \equiv \epsilon_F - \epsilon_A$, and ϵ_A is assumed to be -0.73 eV. (The zero of energy is at the conduction band.)

the curve. Other distributions, such as a normal distribution centered at about $K=0.5$, could be considered also, but it is doubtful that any physically reasonable distribution would significantly change the result for ϵ_A .

Thus, we have fairly well established that a deep level at 0.73 eV from the conduction band (or 0.69 eV from the valence band) is controlling the Fermi level at room temperature. The only established energy levels in this region are due to Cr and O. However, O-doped samples are, in general, more conductive than Cr-doped samples and rarely have a room-temperature Fermi level much greater than 0.60 from the conduction band.¹³ Therefore, we believe that the level we have measured is due to Cr. The role of the shallower O, in our model, would simply be to influence the values of K .

It is tempting to compare this value of ϵ_A with the same value deduced earlier from p -vs- T measurements.² However, it must be remembered that p -vs- T measurements give essentially a $T=0^\circ\text{K}$ value. Furthermore, this type of measurement has been performed on several other GaAs:Cr samples in this laboratory, and the results include ϵ_A 's as high as 0.77 eV, with a mean of about 0.74 eV (from the valence band), near midgap at $T=0^\circ\text{K}$. The simplest explanation of all of these data is that there is an energy level, due to Cr, which remains near the center of the gap as the temperature is changed. This does not preclude, of course, the existence of other levels due to Cr.

Recently, Ashby *et al.*¹⁴ have studied the tempera-

ture dependences of the Ohmic and space-charge-limited currents in a Cr-doped LEC crystal and concluded that the room-temperature Fermi level is controlled by two levels, at 0.40 and 0.98 eV from the conduction band. The concentrations of these two levels were calculated to be 5×10^{12} and $1.5 \times 10^{15} \text{ cm}^{-3}$, respectively, and the latter level was attributed to Cr. In regard to this, we first note that it would be virtually impossible to explain the relatively narrow ϵ_F range near midgap, in our wide variety of samples, by two levels so far from midgap. Second, as will be seen later, mass-spectrographic data show at least one to two orders of magnitude higher Cr concentrations in *all* of our samples than that calculated for theirs. In fact, a Cr concentration of $1.5 \times 10^{15} \text{ cm}^{-3}$ would not be sufficient to compensate the shallow donors in most bulk crystals. Finally, in results from about 10 samples, we have never seen a *decrease* in the slope of ρ -vs- T data at high temperatures ($\sim 400^\circ\text{K}$) as was observed by Ashby *et al.* for their sample. We conclude that their sample was probably not typical of ours, and we reaffirm our belief that, for our samples, the dominant level is near the middle of the gap.

IV. MASS-SPECTROSCOPY RESULTS

For each sample, the SSMS analysis¹⁵ was carried out on a crystal taken from the same wafer, an adjacent wafer in the boule, or, in some cases, from the same crystal as that used for electrical measurements. The detected impurities were B, C, N, O, F, Mg, Al, Si, P, Te, S, Cl, K, Ca, Ti, Cr, Fe, and Ni. All other impurities, except possibly for H, Ta, Au, and Na, had concentrations $< 0.5 \times 10^{16} \text{ cm}^{-3}$. It is known¹⁶ that Si, Te, and S are generally shallow donors (N_D), C, Mg, Fe, and Ni are shallow acceptors (N_A), O is a deep donor (N_{DD}), and Cr is a deep acceptor (N_{AA}). (Here, "shallow" is with respect to the Fermi level, which is near midgap). From photoconductivity measurements,¹³ it can be deduced that the room-temperature energy level for O lies at about 0.68 eV from the conduction band. Then, if degeneracy factors of $\frac{1}{2}$ and 4 are assumed for the monovalent O and Cr centers, respectively, we can calculate the ionized fractions of these centers: $N_O^+ \approx N_O [1 + 2 \exp(\epsilon_F + 0.68)/0.0255)]^{-1}$, and $N_{Cr}^- \approx N_{Cr} [1 + 4 \exp(-0.73 - \epsilon_F)/0.0255)]$, where we have assumed $\epsilon_C = 0$. Since $N_D^+ \approx N_D$ and $N_A^- \approx N_A$, we can calculate the expected concentration of ionized impurities: $N_I \approx N_D^+ + N_{DD}^+ + N_A^- + N_{AA}^-$. There is, of course, some uncertainty in the O and Cr energy levels and the degeneracy factors, but we believe that the uncertainties in the SSMS results themselves are far more important. The results are given in Table III and Fig. 3, with N_A , N_D , N_{AA} , and N_{DD} made up from the particular impurities designated above.

It is important to be able to judge the validity of N_I determined in this manner because we have ignored the following possibly important considerations: (1) ionized native defects, such as Ga or As vacancies; (2) clusters of impurities, which would probably reduce the overall impurity scattering; (3) the amphoteric nature of Si and C, which, however, would not reduce the total N_I ; (4) complexes, which may or may not be charged; (5) multiply charged impurities. Furthermore, SSMS

TABLE III. Mass-spectrographic results for the GaAs samples used in this study (all units are 10^{16} cm^{-3}).

Sample	N_{Tot}	N_A	N_D	N_{AA}	N_{DD}	$N_A^+ + N_{AA}^-$	$N_D^+ + N_{DD}^-$	N_I
A ₁	38.8	3.4	1.3	8.8	14.6	6.4	9.1	15.5
A ₂	29.9	8.4	5.7	8.4	13.3	12.6	10.6	23.2
A ₃	71.3	3.3	19.7	29.2	16.4	9.5	31.0	40.5
A ₄	86.1	11.9	33.2	15.2	26.1	17.7	46.3	64.0
B ₁	55.2	9.2	14.2	2.4	7.5	10.9	17.5	28.4
B ₂	35.4	9.6	7.5	4.9	4.4	11.9	9.3	21.2
C ₁	58.5	8.5	6.4	8.0	13.3	12.9	10.8	23.7
C ₂	123.7	12.4	11.5	79.7	12.8	38.5	18.6	57.1
C ₃	37.9	13.3	9.2	8.4	7.1	19.3	12.0	31.3
C ₄	...							
D ₁	114.4	29.7	11.0	2.4	38.7	32.0	12.6	44.6
E ₁	36.9	9.3	5.3	4.4	13.7	12.0	13.4	25.4
E ₂	58.6	14.3	16.8	12.8	7.5	19.9	20.4	40.3
F ₁	14.0	3.7	3.1	3.8	1.8	5.6	3.8	9.4
F ₂	39.8	16.0	5.3	6.6	8.8	19.5	8.4	27.9
F ₃	59.3	15.8	10.2	18.6	5.3	34.2	10.2	44.4
F ₄	75.4	17.7	16.7	9.3	15.0	21.7	18.0	39.7
G ₁	18.2	5.3	2.0	2.4	6.2	6.5	4.2	10.7
G ₂	21.3	5.3	3.8	4.4	4.9	8.4	4.7	13.1
H ₁	66.9	15.8	11.5	20.8	8.4	23.0	16.0	39.0
H ₂	23.5	2.8	2.7	12.4	3.7	6.1	5.0	11.1
H ₃	25.1	5.3	2.5	7.5	2.5	7.9	3.8	11.7

results on individual elements can be in error by as much as a factor 2–3, although the relative error in N_I will not be as large, since N_I , in our analysis, is a sum of the contributions from nine elements. Fortunately, to determine the accuracy of N_I , we have at least three checks. The first criterion that must be satisfied is $N_D + N_{DD} > N_A$, or else the sample would be low-resistivity (i.e., $\rho \ll 10^7 \Omega \text{ cm}$) p type. The second criterion is $N_A + N_{AA} > N_D$, or the sample would be low-resistivity n type. The third criterion is from charge conservation, $N_D^+ + N_{DD}^- = N_A^+ + N_{AA}^-$, since n and p are negligible. Only three samples, F₂, F₃, and H₃, violate the first criterion, and only B₁ violates the second criterion, as seen in Table III. In all four of these cases, the criteria are just barely violated.

The third criterion, that of charge conservation, allows us to establish *minimum* errors for the N_I ; i.e., $\Delta N_I^{\text{min}} \approx |(N_A^+ + N_{AA}^-) - (N_D^+ + N_{DD}^-)|$. The error bars shown in Fig. 3 are obtained in this way. It may be noted that $\Delta N_I^{\text{min}}/N_I < 50\%$ for all but one of the samples.

To check the SSMS repeatability, we had three samples from the same wafers as E₂, B₁, and B₂, respectively, analyzed on the same spectrometer. In each case, most of the elements of concentration greater than 1 ppmA ($4.4 \times 10^{16} \text{ cm}^{-3}$) repeated to within a factor of 2, and the total N_I was within 50%. For trace elements of concentration less than 1 ppmA, however, the discrepancies were often much greater.

There are several possible reasons for this, including mass-spectrometer contamination or inhomogeneous distribution of impurities within a wafer.

Independent mass-spectrographic results on A₁–A₄ were obtained in a different laboratory, and most of the elemental concentrations agreed to within a factor of 2 (an important exception was Si). Also, independent SSMS and SIMS (secondary-ion mass spectroscopy) results on samples B₁ and B₂ showed much less Si and Cr than measured in our study. It is difficult to know whether spectrometer contamination or the lack of good standards is the principal reason for these discrepancies.

To relate N_I to electron mobility we use the Conwell-Weisskopf formula.¹⁷ (The more commonly used Brooks-Herring relationship¹⁸ is not applicable at these low carrier concentrations.) By using the known values of the effective mass and dielectric constant, we get, at room temperature,

$$\mu_I \approx \frac{7.38 \times 10^{21}}{N_I \ln(1+x^2)}, \quad x^2 = \frac{3.42 \times 10^{13}}{N_I^{2/3}}. \quad (13)$$

Then, in Matthiessen's approximation, we calculate $\mu^{-1} = \mu_I^{-1} + \mu_L^{-1}$, where the lattice-limited mobility is taken to be $\mu_L \approx 8000 \text{ cm}^2/\text{V sec}$.¹⁹ A plot of Eq. (13) is shown in Fig. 3, along with the experimental values of μ_n (from electrical measurements) and N_I (from SSMS). Typically, the probable error in μ_n is less than 10%, while the *minimum* error in N_I is shown by an error

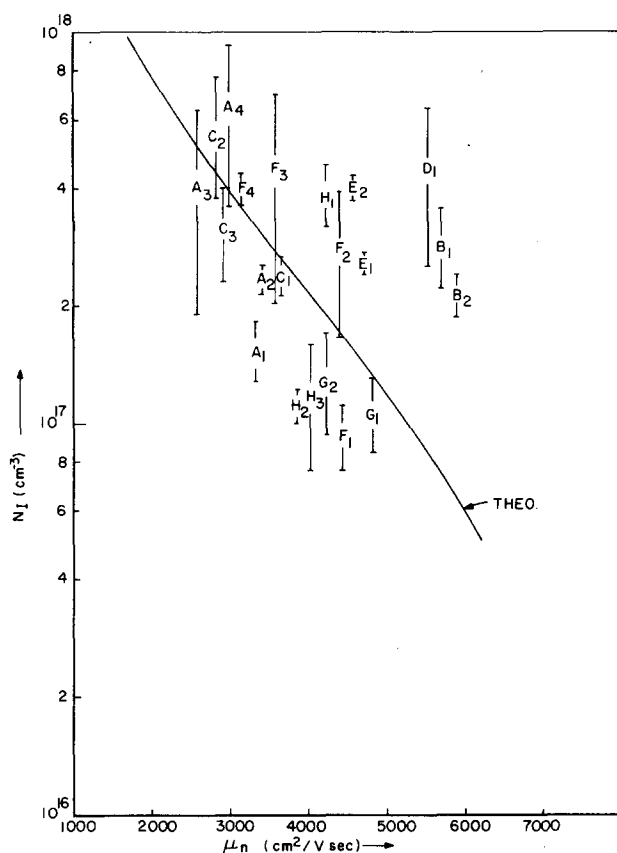


FIG. 3. The total ionized-impurity concentration N_I deduced from mass-spectrographic measurements versus the calculated electron mobility μ_n . The symbols correspond to the sample designations given in Table I. The theoretical line is calculated by combining ionized-impurity scattering and lattice scattering ($\mu_L \approx 8000 \text{ cm}^2/\text{V sec}$) according to Matthiessen's rule.

bar. The theoretical curve itself can be in error by several tens of percent due to the approximations in the Conwell-Weisskopf theory and to the use of Matthiessen's rule. Another consideration, the Hall factor, is probably within 10% of unity at these impurity levels.²⁰

Although the correlation between the experimental data and the theoretical line in Fig. 3 is not high, still the line seems to run reasonably well through the middle of the points, and it should be remembered that no "fitting" parameters were employed to accomplish this. Samples falling well above the line, such as D_1 , B_1 , and B_2 , could have impurity clustering and precipitates, which would make their true N_I 's lower than those deduced from the SSMS data. However, as mentioned earlier, independent SSMS results gave significantly lower N_I 's for samples B_1 and B_2 , so that they probably should lie closer to the line anyway.

It may also be noted that, within the samples of a given manufacturer, the expected inverse relationship between μ_n and N_I generally holds. For example, samples A_1 and A_2 were wafers taken from one end of their respective Czochochalski boules, and A_3 and A_4 from

the other end. Both μ_n and N_I here reflect the expected uneven incorporation of impurities in such boules.

V. CONCLUSIONS

We have shown that good values of n and μ_n may be obtained for most semi-insulating GaAs:Cr crystals by use of a mixed-conductivity analysis. Attempts to obtain these parameters from simple Hall-effect analyses require complicated models with additional assumptions.^{21,22} We have also shown, from a Fermi-level analysis, that the dominant room-temperature Cr level in the semi-insulating crystals lies at 0.69 ± 0.02 eV from the valence band. Other Cr levels may exist too, of course. We have also measured a good value for the intrinsic carrier concentration $n_i = (1.7 \pm 0.4) \times 10^6 \text{ cm}^{-3}$, which agrees well with the theoretical value. Finally, we have examined the relationship between μ_n and N_I , the latter determined from SSMS measurements; the conclusion here is that μ_n is a fairly reliable indicator of N_I . The SSMS results for the total N_I are generally repeatable to within about 50%, but the results for individual elements of concentrations less than 1 ppmA are sometimes not repeatable to within even a factor of 3.

¹J. Barrera, in *Proc. of the Fifth Biennial Cornell Electrical Engineering Conference* (Cornell U.P., Ithaca, 1975), p. 135.

²D.C. Look, *J. Phys. Chem. Solids* **36**, 1311 (1975).

³A. Th. Philadelphus and P.C. Euthymiou, *J. Appl. Phys.* **45**, 955 (1974).

⁴Samples were purchased from Laser Diode Laboratories, Metuchen, N.J., Crystal Specialties, Inc., Monrovia, Calif.; Varian Associates, Palo Alto, Calif., Sumitomo Electric, San Francisco, Calif., and Morgan Semiconductors, Garland, Tex. Other samples studied were grown at the Naval Research Laboratories, Hewlett-Packard, and Monsanto. Because of the proprietary nature of some of the information, none of the samples discussed in this report will be identified by manufacturer.

⁵See, e.g., E.H. Putley, *The Hall Effect and Semiconductor Physics* (Dover, New York, 1968), Chap. 2.

⁶I. Inoue and M. Ohyama, *Solid State Commun.* **8**, 1309 (1970).

⁷J.D. Wiley, in *Semiconductors and Semimetals*, Vol. 10, edited by R.K. Willardson and A.C. Beer (Academic, New York, 1975), Chap. 2, p. 154. Note that the samples tabulated in this reference were more conductive than ours, and the Brooks-Herring formula was used to calculate the theoretical line. However, the use of the Conwell-Weisskopf formula leads to similar results.

⁸D.D. Sell and H.C. Casey, Jr., *J. Appl. Phys.* **45**, 800 (1974).

⁹See, e.g., E.H. Putley, Ref. 5, p. 109.

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¹¹H.J. Hovel, in *Semiconductors and Semimetals*, Vol. 11, edited by R.K. Willardson and A.C. Beer (Academic, New York, 1975), p. 80.

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- ¹⁴A. Ashby, G.G. Roberts, D.J. Ashen, and J.B. Mullin, *Solid State Commun.* **20**, 61 (1976).
- ¹⁵The SSMS results were obtained from Micro-Trace Analytical Services, Industry, Calif.
- ¹⁶For a compilation of electrically active impurities in GaAs, see A.G. Milnes, *Deep Impurities in Semiconductors* (Wiley, New York, 1973), p. 47.
- ¹⁷E. Conwell and V. F. Weisskopf, *Phys. Rev.* **77**, 388 (1950).
- ¹⁸See, e.g., Ref. 9, p. 146.
- ¹⁹Neutral impurities are not taken into account here because most of them would be deep centers, near E_F . Such deep centers should have tightly bound wave functions and thus less scattering power than shallow neutral centers. This fact was not considered in Ref. 2.
- ²⁰For a discussion of the Hall factor in samples for which the Brooks-Herring formula is applicable, see D.L. Rode, in Ref. 7, p. 71.
- ²¹P. F. Lindquist, *J. Appl. Phys.* **48**, 1262 (1977).
- ²²R. Zucca, *J. Appl. Phys.* **48**, 1987 (1977).